Quality Procedure Interim Change Notice

Effective Date: **12/1/03**

5 Page(s)

Section 1: Description of Change (Requester completes)	1. Document Catalog No.: **ER2003-0665**	
2. QP & Rev. No.: **SOP-15.06, R1**	3. ICN No.: **1**	4. QP Title: **Routine Validation of Gamma Spectroscopy Data**

5. Description of Change:

Section 6.2, step 2:

1) Delete 1st row in table and change "< the MDC" (1st colume) to "≤ the MDC."

2) Step 3: delete row one and change second row from "<3 times" to "≤3 times."

3) Add the following text and table after step 4:

"Reference the following table as applicable."

MDC VALUE	SAMPLE VALUE	UNCERTAINTY VALUE	FU4 QUALIFIER REASON CODE
0	0	0	R, R5b
0	0	NULL	R, R5b
NULL	X-VALUE	0	R, R5a
NULL	0	0	R, R5a

4) Change Attachment B, page 24, 3rd row, Reason Code R5, Description: "The results for the affected analytes are considered not detected (U) because the associated sample concentration was less than or equal to the MDC."

5) Change Attachment B, page 25, 7th row, Rad R11: "Results of the affected analytes are considered not detected (U) because the associated sample concentration was less than or equal to three times the total propagated uncertainty."

6) Change Attachment D, page 27, number 2. as follows: "Sample result is ≤MDC."

7) Change Attachment D, page 27, number 3. as follows: "Sample result is ≤3 times the TPU calculation."

6. Attachments Modified, Added, or Removed:	☒ Yes	☐ No

7. ICN Justification:
Updating SOP to address MDA/sample value/uncertainty changes.

8. Requester: Nita Patel   [Signature on file.]   11/20/03
(Print name, then sign.)   (Date)

Section 2: Evaluation and Approval (PTL, Technical Reviewer, and QPPL complete.)

9. Evaluation Remarks: (If none, enter N/A) N/A

10. Project Team Leader: Sheila Zhang   [Signature on file.]   11/24/03
(Print name, then sign.)   (Date)

11. Technical Reviewer: Keith Greene   [Signature on file.]   11/20/03
(Print name, then sign.)   (Date)

12. QPPL: Larry Maassen   [Signature on file.]   11/25/03
(Print name, then sign.)   (Date)

QP-4.1, R5

Los Alamos National Laboratory
RRES-Remediation Services Project

Attachment B: Gamma Spectroscopy Data-Validation Reason Codes

Code	Rad	Qualifier Nondetects	Qualifier Detects	Description	Comments
4	R4	R (See comments)	R (See comments)	Required method blank documentation is missing. Validation cannot proceed without this information.	Package should be returned to the SMO or the information requested from the laboratory.
4a	R4a	N/A	U	Results for the affected analytes are considered not detected (U) because the associated sample concentration was less than 5 times the amount in the method blank.	
5	R5	U	U	Results for the affected analytes are considered not detected (U) because the associated sample concentration was less than or equal to the MDC.	
5a	R5a	R (See comments)	R (See comments)	MDC documentation is missing. Validation cannot proceed without this information.	Package should be returned to the SMO or the information requested from the laboratory.
5b	R5b	R	R	Results for the affected analytes are rejected (R) because spectral interference prevents positive identification of the analytes.	
6	R6	R (See comments)	R (See comments)	LCS documentation is missing. Validation cannot proceed without this information.	Package should be returned to the SMO or the information requested from the laboratory.
6a	R6a	N/A	J+	Results for the affected analyte are considered estimated and biased high (J+) because the associated LCS was greater than 120%R.	Qualify only detected results.
6b	R6b	R	R	Results/reporting limits for the affected analytes should be regarded a rejected (R) because the associated LCS was less than 10%R.	
6c	R6c	N/A	J-	Results for the affected analyte are considered estimated and biased low (J-) because the associated LCS was less than 80%R but greater than or equal to 10%R.	Code is used for detected analytes.
6d	R6d	UJ	N/A	Reporting limits for the affected analyte are considered estimated (UJ) because the associated LCS was less than 80%R but greater than or equal to 10%R.	Code is used for nondetected analytes.
7	R7	UJ	J	Duplicate documentation is missing. Validation can proceed without this information with qualification.	Package should be returned to the SMO or the information requested from the laboratory.
7b	R7b	N/A	J	Results for the affected analytes are qualified as estimated (J) because the associated duplicate sample has a DER greater than or equal to 2 but less than or equal to 4.	
7c	R7c	N/A	R	Results for the affected analytes are qualified as rejected (R) because the associated duplicate sample has a DER greater than 4.	
9	R9	UJ	J-	Results/reporting limits for the affected analytes are considered estimated and biased low (J-)/estimated (UJ) because the extraction holding time was exceeded.	
9a	R9a	R	R	Results for the affected analytes are considered rejected (R) because the sample extraction exceeded 2 times the method published holding time.	

Code	Rad	Qualifier Nondetects	Qualifier Detects	Description	Comments
11	R11	N/A	U	Results for the affected analytes are considered not detected (U) because the associated sample concentration was less than or equal to three times the total propagated uncertainty.	Code should only be used after checking the detection status for results greater than the MDC except in cases where an MDC was not provided.
19	R19	(See comments)	(See comments)	Validator identified quality deficiencies in the reported data that require qualification. Please see the Data-Validation Cover Sheet for specific details.	Apply the appropriate qualifier to identify the effect of the quality deficiency on the reported data.

Attachment D: Gamma Spectroscopy Data-Validation Checklist

Yes	No	n/a	(check one)	Assign qualifier listed below if criteria = Yes	
				Detected analyte	Undetected analyte
☐	☐	☐	1. MDC and/or TPU were not stated for each radionuclide in each batch for each sample.	a	a
☐	☐	☐	2. Sample result is ≤MDC.	U, R5	U, R5
☐	☐	☐	3. Sample result is ≤3 times the TPU calculation.	U, R11	N/A
☐	☐	☐	4. Sample results are tentative because of spectral interference.	R, R5b	R, R5b
☐	☐	☐	5. Preparation/method blank is not reported.	R, R4	R, R4
☐	☐	☐	6. Analyte detected in blank and sample result for analyte =5x the amount in blank	U, R4a	N/A
☐	☐	☐	7. Duplicate analysis information is not present.	J, R7	UJ, R7
☐	☐	☐	8. DER for detected analytes is =2 but =4.	J, R7b	N/A
☐	☐	☐	9. DER for detected analytes is >4.	R, R7c	N/A
☐	☐	☐	10. Laboratory Control Sample (LCS) information is not present.	R, R6	R, R6
☐	☐	☐	11. LCS % recovery is >120%.	J+, R6a	N/A
☐	☐	☐	12. LCS % recovery is <80 but =10%.	J-, R6c	UJ, R6d
☐	☐	☐	13. LCS % recovery is <10%.	R, R6b	R, R6b
☐	☐	☐	14. Sample was extracted outside of the appropriate hold time.	J-, R9	UJ, R9
☐	☐	☐	15. Sample was extracted >2 times the appropriate holding time.	R, R9a	R, R9a
☐	☐	☐	16. Other obvious data quality issues identified.	__, R19	__, R19

a If the laboratory cannot provide the missing MDC, an estimated MDC can be calculated using 3 times the TPU.

Risk Reduction and Environmental Stewardship—Remediation Program

Standard Operating Procedure

for **Routine Validation of Gamma Spectroscopy Data**

Revision Log

Revision No.	Effective Date	Prepared By	Description of Changes	Affected Pages
R0	07/20/00	Bart Vanden Plas	Initial Procedure.	All
R1	05/20/03	Kim Hejde	Rewritten to streamline and update process.	All

Table of Contents

Routine Validation of Gamma Spectroscopy Data

1.0   PURPOSE

1.1   This standard operating procedure (SOP) represents the minimum standards for evaluating gamma spectroscopy data generated for the Los Alamos National Laboratory (LANL), Risk Reduction and Environmental Stewardship—Remediation Program (RRES-R) for samples analyzed for gamma-emitting isotopes using the methods required under the current statement of work (SOW) for analytical services. The evaluation of data by this procedure is not specific to a particular data use. However, this procedure may be used to develop focused data-validation requirements specific to a particular data use.

1.2   Implementation of this procedure results in a tabulation of data compliances and noncompliances identified relative to expectations based on national guidelines (U.S. Environmental Protection Agency [EPA] 1994, 48639) for data review. Data noncompliance is noted through the application of qualifiers (Attachment A) and reason codes (Attachment B) to the reported results. Because the EPA guidelines are specific to analyses for inorganic chemicals, additional guidance (ANSI 1996, Currie 1968, Fong and Alvarez 1996, MARSSIM 1997, and LANL 2000) was used in the preparation of this SOP. Because the acceptance criteria used for this procedure are not based on site-specific acceptance criteria, the results of this validation procedure are intended to be used as general indicators of data quality and should not be construed as a definitive identification of data usability.

1.3   Nothing in this SOP precludes the validator from going beyond the minimum requirements specified in this SOP. To address data quality issues in a data package, the validator may assign qualifiers based on his or her professional judgment. Implementation of this procedure may be followed by a more focused and data use-specific evaluation of data, especially if implementation of this SOP indicates that technical deficiencies may exist in the data.

1.4   The validator shall indicate any need for a more focused validation on the Data-Validation Cover Sheet (Attachment C).

1.5   The validator shall use the Gamma Spectroscopy Data-Validation Checklist (from now on known simply as the Data-Validation Checklist; Attachment D) to record the specific validation steps conducted.

2.0 SCOPE

2.1 All **RRES-R personnel** shall implement this mandatory SOP when evaluating gamma spectroscopy data generated for the RRES-R Program.

2.2 Subcontractors performing work under the RRES-R Program's quality program shall follow this SOP.

3.0 TRAINING

3.1 **RRES-R personnel** shall train to and use the current version of this SOP; contact the author if the SOP text is unclear.

3.2 **RRES-R personnel** using this SOP shall document training in the RRES-R training database located at http://erinternal.lanl.gov/Training/login.asp in accordance with QP-2.2.

3.3 The responsible **supervisor** shall monitor the proper implementation of this procedure and ensure that the appropriate personnel complete all applicable training assignments.

3.4 All **data validators** (from now on known as "validators") who implement this SOP shall possess a minimum of a bachelor's degree in chemistry or one of the physical sciences.

3.5 All **validators** shall have two years experience in generating analytical data in an environmental or radiochemistry analytical laboratory or two years of data-validation experience that includes the production or validation of gamma spectroscopy data.

3.6 All **validators** who are new to this SOP shall work under the direct supervision of an experienced RRES-R Program validator who reviews and signs data packages until ten data packages for each analytical suite are satisfactorily validated.

3.7 All **validators** shall demonstrate familiarity with the EPA national functional guidelines for data review.

4.0 DEFINITIONS

4.1 *Activity concentration*—Level of radioactivity per unit volume or mass measured as a concentration; usually reported in pCi/g or pCi/L.

4.2 *Analyte*—Element, nuclide, or ion that a chemical analysis seeks to identify and/or quantify; the chemical constituent of interest.

4.3 *Annihilation radiation*—The two gamma rays of 0.511 MeV energy that are emitted as a result of the combination and disappearance of an electron and a positron.

4.4   *a posteriori*—In this SOP, defined as "after the measurement."

4.5   *a priori*—In this SOP, defined as "before the measurement."

4.6   *Blank sample*—Sample expected to have negligible or immeasurable amounts of analytes. Results of blank-sample analyses indicate whether field samples might have been contaminated during the sample collection, transport, storage, preparation, or analysis process.

4.7   *Data validator*—Person who has met the minimum standards of training established by the RRES-R Program for data validation and performs data validation on behalf of the RRES-R Program.

4.8   *Detect (radionuclides)*—Sample result greater than the minimum detectable concentration (MDC) reported by the analytical laboratory. The laboratory reports the concentration of the analyte in the sample.

4.9   *Detector background*—Ambient signal response recorded by radioactivity measuring instruments that is independent of radioactivity contributed by the radionuclides being measured in the sample.

4.10   *Duplicate analysis*—Analysis performed on one of a pair of identically prepared subsamples taken from the same sample. The subsamples can be created in the field (field duplicate samples) or in the laboratory (laboratory duplicate samples).

4.11   *Duplicate error ratio (DER)*—Measurement of the precision of analytical laboratory duplicate samples in a batch. The DER is based on the standard deviations of the sample and the duplicate sample.

$$DER = \frac{\left| S - R \right|}{\sqrt{u_S^2 + u_R^2}} \ ,$$

where

DER = duplicate error ratio,

   S = sample value,

   R = duplicate value,

  u_S = sample uncertainty, and

  u_R = duplicate uncertainty.

If DER <2, then the sample and duplicate are not statistically different at the 95% confidence level.

Note: The DER value is based on 1σ. The validator should pay particular attention to the reporting practices of the laboratory and adjust the DER value accordingly (for example, if the laboratory reports the uncertainties as 2σ, the DER value should be recalculated using 1σ). The DER should

also be calculated using a true duplicate and not by the reanalysis of the same sample.

4.12   *Form 1*—Organic analysis data sheet for each individual sample that includes information needed to identify the sample and its analytical results.

Note: See the SOW for analytical services (RFP No. 9-XS1-Q4257) for a more complete definition.

4.13   *Gamma spectroscopy data*—Analytical results and associated data for samples analyzed for gamma-emitting isotopes.

Note: Routine validation of gamma spectroscopy is included in this SOP and not in SOP-15.07 because of the greater complexity of gamma spectroscopy data.

4.14   *Holding time*—Maximum elapse of time that a sample can be stored without unacceptable changes in analyte concentrations. Holding times apply under prescribed conditions; deviations from these conditions may affect the holding time. Extraction holding time refers to the time lapse from sample collection to sample preparation. Analytical holding time refers to the time lapse between sample preparation and analysis.

4.15   *Laboratory control sample (LCS)*—Known matrix that has been spiked with compound(s) representative of the target analytes. The LCS is used to document laboratory performance. The acceptance criteria for LCSs are method specific.

4.16   *Laboratory duplicate sample*—Portions of a sample taken from the same sample container, prepared for analysis and analyzed independently but under identical conditions. Duplicate samples are used to assess or demonstrate acceptable laboratory method precision at the time of analysis. Each duplicate sample is equally representative of the original material. Duplicate analyses also are performed to generate data to determine the long-term precision of an analytical method on various matrices.

4.17   *LANL data-validation qualifiers*—Data qualifiers defined by LANL and used in the RRES-R Program routine validation process. Attachment A lists all the data qualifiers that are applicable to all analytical suites.

4.18   *LANL data-validation reason codes*—Codes applied to the sample data by data validators who are independent of the contract laboratory that performed the sample analysis. Reason codes provide an in-depth and analysis-specific explanation for applying the qualifier along with a description of the potential impact on the data use. For a complete list of

data qualifiers applicable to any particular analytical suite, consult the appropriate RRES-R Program SOP.

4.19 *Matrix spike*—An aliquot of a sample spiked with a known concentration of target analyte(s). Matrix-spike samples are used to measure the ability to recover prescribed analytes from a native sample matrix. Spiking typically occurs before sample preparation and analysis.

4.20 *Minimum detectable concentration*—Minimum activity concentration that the analytical laboratory equipment can detect in 95% of the analyzed samples. That is, if the actual concentration of a sample is above the MDC, a less than 5% chance exists that the measured concentration will fall below the decision level concentration (DLC) and result in a "nondetect." An MDC measures analytical performance (not detection limits),

$$MDC = C \times \left(2.71 + 4.65\sqrt{N_b}\right),$$

where

$MDC =$ the minimum detectable concentration reported in pCi/g or pCi/L;

$C =$ a group of factors that convert counts to an activity concentration (C is omitted if N_b is expressed in concentration units);

$2.71 = 1.65^2$ (165 normal probability, one sided, for 0.05 significance);

$4.65 = 1.65 \times 2(2)^{0.5}$;

$N_b =$ total analyte-free blank (or background) counts, and all blank, background, and sample count times are equal.

4.21 *Nondetect (radionuclides)*—Sample result that is less than the MDC.

4.22 *Percent recovery (%R)*—Amount of material detected in a sample (minus any amount already in the sample) divided by the amount added to the sample and expressed as a percentage.

4.23 *Precision*—Concept used to describe the dispersion of measurements. Precision may be absolute or relative to a particular measure of central tendency. The mathematical formulas used to determine precision vary according to the problem at hand.

4.24 *Preparation blank*—An analyte-free matrix to which all reagents are added in the same volumes or proportions as those used in environmental sample processing and which is prepared and analyzed in the same manner as the corresponding environmental samples. The preparation blank is used to assess the potential for contamination of samples during preparation and analysis.

4.25   *Request number (RN)*—An identifying number assigned by the RRES-R Program to a group of samples that are submitted for analysis.

4.26   *Routine data*—Data generated using analytical methods that are identified as routine methods in the current RRES-R Program SOW for analytical services.

4.27   *Routine data validation*—Process of reviewing analytical data relative to quantitative routine acceptance criteria. The objective of routine data validation is two-fold: (1) to estimate the technical quality of the data relative to the minimum national guidelines adopted by the RRES-R Program, and (2) to indicate to data users the technical data quality at a general level by assigning qualifier flags to environmental data whose quality indicators do not meet acceptance criteria.

4.28   *Sigma (s)*—Standard deviation (square root of the variance) of a set of measurements. For normally distributed data, a range of one sigma (1σ) below the estimated mean to one sigma (1σ) above the estimated mean signifies a 67% confidence that the mean of a population lies within that range. Similarly, a range of plus/minus 2 sigma ($\pm 2\sigma$) implies 95% confidence that a population mean lies within that range.

4.29   *Target analyte*—An element, chemical, parameter, concentration, mass, or magnitude that is designed to be quantified by use of a particular test method.

4.30   *Total propagated uncertainty (TPU)*—Sum of all aspects of uncertainty introduced throughout the sample analysis process from sample collection to reporting of results. Many aspects of TPU may be specifically calculated by an analytical laboratory (for example, net instrumental error and counting uncertainty). Other aspects of TPU may not be quantifiable (for example, heterogeneity of concentrations at site), and thus, cannot be directly included in a laboratory's estimate of TPU.

5.0   RESPONSIBLE PERSONNEL

The following personnel are responsible for activities identified in this procedure:

- Data Validator (see definition 4.7)
- RRES-R Personnel
- Supervisor
- User

6.0 PROCEDURE

The **Validator** shall perform the following actions unless otherwise noted. Make any deviations from this SOP in accordance with QP-5.7 and/or SOP-01.01.

6.1 Preparing for Data Validation

1. Obtain the required current versions of the Gamma Spectroscopy Data-Validation Checklist (Attachment D) from the RRES-R Program website (http://erinternal.lanl.gov/Quality/ user/forms.asp).

2. Obtain from the Sample Management Office (SMO) of the Field Support Facility (FSF) the data-record packages that contain the sample data to be validated.

3. Prepare a Data-Validation Cover Sheet (see Attachment C) by completing the top part of the cover sheet and placing a check or other mark adjacent to the analytical suites for which this validation is being performed.

4. If any data are rejected, check the rejected box and notify the project chemist immediately.

5. Verify that the following items are present in the data-record package:

   - Signed LANL COC record

   - Case narrative

   - Result forms (Contract Laboratory Program [CLP] Form 1 or equivalent for each sample)

   - QC Forms (CLP form equivalents) for water and/or soils, as appropriate

   - The instrument readout (raw data) for the samples

6.

IF the required documentation for the data-record package is…	FOR…	THEN…
Complete,		• Go to Step 8.
Missing,	< 6 mo.	• Contact the analytical laboratory and/or the SMO. • Allow 3 business days for submittal. • Go to Step 7.

6.	**IF the required documentation for the data-record package is…**	**FOR…**	**THEN…**
	Missing,	= 6 mo.	• Contact the analytical laboratory and/or the SMO. • Allow 10 business days for submittal. • Go to Step 7.

> **Note:** To expedite the validation process, the validator should request that the laboratory forward the missing information via email or fax directly to the validator within 24 h of notification.

7.	**IF the analytical laboratory…**	**THEN…**
	Submits the documentation within the specified time period,	• Go to Step 8.
	Does <u>not</u> submit documentation within the specified time period,	• Notify the SMO for contract-compliance action. • Go to Step 8.

8. In the Data-Validation Cover Sheet "Completeness Check" section,

   A. Record the presence or absence ("Yes" or "No") of each item, as appropriate.

   B. Indicate under the Comments/Problems section any samples whose data are missing from the data-record package.

9. Photocopy the following items:

   • Chain of custody forms

   • Form 1 from the analytical laboratory (used during the validation process)

   > **Note:** Do <u>not</u> record the data-validation qualifiers and the reason codes on the original form (Form 1).

   > **Note:** The validator must submit the photocopies of the items listed in Sections 6.1.10 through 6.1.12 as attachments to the completed Gamma Spectroscopy Data-Validation Checklist. Each Form 1 must be initialed and dated by the validator; these initials and

date must be present even if the validator accepts laboratory qualification.

6.2   Statistically Validating the Sample Results

Note: In any instance that the required information is missing, notify the analytical laboratory and/or SMO to obtain the information before proceeding with the validation process.

Note: Section 6.2 applies to all gamma spectroscopy nuclides (both COPCs and non-COPCs). The statistical analysis must be performed first to determine the detection status for the target nuclides before completing the subsequent steps in this validation procedure.

$$\text{MDC} = C \times \left(2.71 + 4.65\sqrt{N_b}\right). \tag{1}$$

1.

IF…	THEN…
The MDC was stated in the report for each nuclide in each sample in each batch associated with this RN,	• Record "No" on line 1 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Step 2.
<u>Any</u> MDC was <u>not</u> stated in the report for each nuclide in each sample in each batch associated with this RN,	• Notify the SMO and laboratory to request the missing information (see Section 6.1-4). • If the laboratory is unable to provide the missing information, record "Yes" on line 1 of the Gamma Spectroscopy Data-Validation Checklist. • Record the estimated (calculated) MDC for the affected analytes on the individual Form 1 using 3 times the 1-σ TPU of the sample result. • Go to Step 3.

2.

IF the sample value is…	THEN…
= the MDC,	• Record "No" on line 2 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Step 3.
< the MDC,	• Record "No" on line 2 of the Gamma Spectroscopy Data-

2.	IF the sample value is…	THEN…
		Validation Checklist.
		• Qualify all results as undetected (U, R5) on the individual sample Form 1.
		• Record any comments concerning data usability in the Comments/Problems section of the Data-Validation Cover Sheet.
		• Go to Section 6.3, "Verifying Method-Blank Results."

3.	IF the sample value is…	THEN…
	= 3 times the 1 σ Total Propagated Uncertainty (TPU),	• Record "No" on line 3 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Step 4.
	< 3 times the 1 σ TPU,	• Record "Yes" on line 3 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the affected detected analytes as undetected (U, R11) on the individual sample Form 1. • Go to Step 4.

4.	IF the sample value is…	THEN…
	<u>Not</u> reported as tentative by the analytical laboratory because of spectral interference,	• Record "No" on line 4 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Section 6.3, "Verifying Method-Blank Results."
	Reported as tentative by the analytical laboratory because of spectral interference,	• Record "Yes" on line 4 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the affected analytes as rejected (R, R5b) on the individual sample Form 1. • Go to Section 6.3, "Verifying Method-Blank Results."

6.3   Verifying the Method-Blank Results

Note: Section 6.3 applies to all gamma spectroscopy analysis methods and analytes (COPCs and non-COPCs).

Note: If additional validation forms are needed to record validation data for more than one blank, make additional copies of the appropriate forms.

1.
IF…	THEN…
All method blank information is present,	• Record "No" on line 5 on the Gamma Spectroscopy Data-Validation Checklist. • Go to Step 2.
Any method blank information is missing,	• Record "Yes" on line 5 on the Gamma Spectroscopy Data-Validation Checklist. • Contact the analytical laboratory and SMO to request the missing information. • If the laboratory is unable to provide the missing information, qualify the affected results as rejected (R, R4) on the individual sample Form 1. • Go to Step 2.

2.
IF the method blank has…	THEN…
No contamination,	• Record "No" on line 6 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Section 6.4, "Verifying the Laboratory Duplicate Results."

3.	**IF the concentration of any analyte in a sample is…**	**THEN…**
	= to 5 times the concentration of that analyte in the corresponding method blank,	• Record "Yes" on line 6 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the affected analytes as undetected (U, R4a) on the individual Form 1. • Go to Section 6.4, "Verifying the Laboratory Duplicate Results."

6.4   Verifying Laboratory Duplicate Results

Note: Section 6.4 applies to only the eight COPCs unless non-COPCs are requested. Verify the presence of the laboratory duplicate using the forms provided by the analytical laboratory.

Note: Find the reported DER in the data-record package for the duplicate and the sample result, or calculate the DER (or RER) as follows:

$$DER = \frac{|S - R|}{\sqrt{u_S^2 + u_R^2}} \ , \tag{2}$$

where

DER = duplicate error ratio,

S = sample value,

R = duplicate value,

u_S = sample uncertainty, and

u_R = duplicate uncertainty.

6.4.1   If DER is less than 2, then the sample and duplicate are not statistically different at the 95% confidence level.

Note: The DER value is based on 1σ. The validator should pay particular attention to the reporting practices of the laboratory and adjust the DER value accordingly (for example, if the laboratory reports the uncertainties as 2σ, the DER value should be recalculated using 1σ). The DER should also be calculated on a true duplicate, not a reanalysis of the same sample.

1.	**IF…**	**THEN…**
	<u>All</u> the duplicate information is <u>present</u>,	• Record "No" on line 7 on the Gamma Spectroscopy Data-Validation Checklist.

1.	**IF…**	**THEN…**
		• Go to Step 2.
	The duplicate information is <u>missing</u>,	• Record "Yes" on line 7 of the Gamma Spectroscopy Data-Validation Checklist.
		• Contact the analytical laboratory and SMO to request the missing information (see Section 6.1-4).
		• If the laboratory cannot provide the missing information, qualify all results as estimated (J, R7/UJ, R7) on the individual sample Form 1.
		Note: If this information is missing, validation can proceed, but please check with laboratory for consistency purposes.
		• Go to Step 2.

2.	**IF the sample and duplicate results for detected analytes have a DER that is…**	**THEN…**
	< 2,	• Record "No" on lines 8 and 9 of the Gamma Spectroscopy Data-Validation Checklist.
		• Go to Section 6.5, "Verifying the Laboratory Control Sample."
	= 2 and = to 4,	• Record "Yes" on line 8 and "No" on line 9 of the Gamma Spectroscopy Data-Validation Checklist.
		• Qualify the detected analytes as estimated (J, R7b) on the individual Form 1.
		• Go to Section 6.5, "Verifying the Laboratory Control Sample."
	> 4,	• Record "Yes" on line 9 and "No" on line 8 of the Gamma Spectroscopy Data-Validation

2.	**IF the sample and duplicate results for detected analytes have a DER that is…**	**THEN…**
		Checklist.
		• Qualify the detected analytes as rejected (R, R7c) on the individual Form 1.
		• Go to Section 6.5, "Verifying the Laboratory Control Sample."

6.5   Verifying the Laboratory Control Sample Results

Note: Section 6.5 applies to only the eight COPCs unless the non-COPCs are requested. Verify the presence of the LCS sample percent recovery (%R) values using forms provided by the analytical laboratory.

1.	**IF the LCS information is…**	**THEN…**
	Present,	• Record "No" on line 10 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Step 2.
	Missing,	• Record "Yes" on line 10 of the Gamma Spectroscopy Data-Validation Checklist. • Contact the analytical laboratory and the SMO to request the missing information (see Section 6.1-4). • If the laboratory is unable to provide the missing information, qualify affected results as rejected (R, R6) on the individual sample Form 1. • Go to Step 2.

2.	**IF…**	**THEN…**
	All LCS %R fall between 80% and 120%,	• Record "No" on lines 10, 11, 12, and 13 of the Gamma Spectroscopy Data-Validation Checklist.

2.

IF…	THEN…
	• Go to Section 6.6, "Verifying the Holding Time."
<u>No</u> LCS %R are > 120%,	• Record "No" on lines 10 and 11 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Step 3.
<u>Any</u> LCS %R is > 120%,	• Record "Yes" on line 11 and "No" on line 10 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the detected analytes as estimated with a potential positive bias (J+, R6a) on the individual Form 1. • Go to Step 3.

3.

IF…	THEN…
<u>No</u> LCS %R are < 80%,	• Record "No" on lines 12 and 13 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Section 6.6, "Verifying the Holding Time."
<u>Any</u> LCS %R < 80% but = 10%,	• Record "Yes" on line 12 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the detected analytes as estimated with a potential negative bias (J-, R6c) and the undetected analytes as estimated (UJ, R6d) on the individual Form 1. • Go to Section 6.6, "Verifying the Holding Time."
<u>No</u> LCS %R is < 10%,	• Record "No" on lines 12 and 13 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Section 6.6, "Verifying the Holding Time."

3.	**IF…**	**THEN…**
	<u>Any</u> LCS %R < 10%,	• Record "Yes" on line 13 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify all the affected analytes as rejected (R, R6b) on the individual Form 1. • Go to Section 6.6, "Verifying the Holding Time."

6.6   Verifying the Holding Time

1.	**IF…**	**THEN…**
	<u>All</u> the samples were analyzed within their holding times,	• Record "No" on lines 14 and 15 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Section 6.7, "Identifying Obvious Quality Deficiencies."
	<u>Any</u> samples were <u>not</u> analyzed within their holding times,	• Record "Yes" on line 14 of the Gamma Spectroscopy Data-Validation Checklist. • Calculate the number of days the holding time was exceeded. • Go to Step 2.

2.	**IF the holding time was…**	**THEN…**
	<u>Not</u> exceeded by 2 times,	• Record "No" on line 15 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the detected analytes as estimated with a potential negative bias (J-, R9) and the undetected analytes as estimated (UJ, R9) on the individual Form 1. • Go to Section 6.7, "Identifying the Obvious Quality Deficiencies."

2.	IF the holding time was…	THEN…
	Exceeded by 2 times,	• Record "Yes" on line 15 of the Gamma Spectroscopy Data-Validation Checklist. • Qualify the affected analytes as rejected (R, R9a) on the individual Form 1. • Go to Section 6.7, "Identifying the Obvious Quality Deficiencies."

6.7   Identifying the Obvious Quality Deficiencies

IF …	THEN…
<u>Any</u> significant or obvious data quality deficiencies are noticed during the data validation process, take the following actions,	• Record "Yes" on line 16 of the Gamma Spectroscopy Data-Validation Checklist. • Contact the analytical laboratory and SMO, if necessary, to resolve the quality issue. • Apply the appropriate qualifier to the data based on best professional judgment and apply reason code R19. • Write a clear description of the quality issue on the Data-Validation Cover Sheet. • Go to Section 6.8, "Assembling the Validation Data-Record Package."
<u>No</u> obvious quality deficiencies outside of those covered by this SOP are noticed,	• Record "No" on line 16 of the Gamma Spectroscopy Data-Validation Checklist. • Go to Section 6.8, "Assembling the Validation Data-Record Package."

6.8   Assembling the Validation Package

Include the following items in order:

• The complete signed, and dated Data-Validation Cover Sheet

- The Gamma Spectroscopy Data-Validation Checklists (completed from Sections 6.2 through 6.7)

- Photocopies of the completed forms (Form 1) on which the data validator recorded the qualifier flags and reason codes

- A photocopy of the data-record chain of custody

6.9 Submitting the Validation Data-Record Package

Submit the data-record package to the SMO, in accordance with LANL-ER-SOP-15.09.

7.0 LESSONS LEARNED

7.1 Before performing work described in this SOP, RRES-R Personnel should go to the Department of Energy Lessons Learned Information Services home page, located at http://www.tis.eh.doe.gov/ll/ll.html, and/or to the LANL Lessons Learned Resources web page, located at http://www.lanl.gov/projects/lessons_learned/, and search for applicable lessons.

7.2 During work performance and/or after the completion of work activities, RRES-R **Personnel**, as appropriate, shall identify, document, and submit lessons learned in accordance with the LANL, Lessons Learned System located at http://www.lanl.gov/projects/lessons_learned/.

8.0 RECORDS

Although no records are submitted to the Records Processing Facility (RPF) in the course of completing this procedure, the items identified in Section 8.5 will be a part of the data-record package submitted to the RPF from the SMO in accordance with SOP-15.09.

9.0 REFERENCES

- ANSI 1996. Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories, ANSI N42.23-1996.

- Currie, L. 1968. "Limits for Qualitative Detection and Quantitative Determination." Analytical Chemistry, March, 1968.

- DOE (U.S. Department of Energy), Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM), Final, Washington, D.C. (DOE 1997, 63128), December 1997.

- U.S. Environmental Protection Agency, "U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review,"

Publication 9240.1-05-01, EPA-540/R-94/013, Office of Solid Waste and Emergency Response, Washington, D.C., February 1994.

- SOP-15.09, Chain of Custody for Analytical Data Packages

- Fong, S., and Alvarez, J. 1997. "Data Quality Objectives for Surface-Soil Cleanup Operation Using In Situ Gamma Spectrometry for Concentration Measurements," Health Physics (Vol. 72, No.2) February 1997.

- LANL (Los Alamos National Laboratory), "Environmental Restoration Project Statement of Work for Analytical Services," Revision 2, RFP Number 9-SX1-Q4257, Los Alamos National Laboratory, Los Alamos, New Mexico. July 1995.

- QP-2.2, Personnel Orientation and Training

- QP-4.2, Standard Operating Procedure Development

- Vanden Plas, B., 2000. "Approach to Gamma Spectroscopy Data Quality Evaluation," Los Alamos National Laboratory LA-UR-00-1088, Los Alamos, New Mexico (ER2000-0061), 2000.

10.0 ATTACHMENTS

The **user** of this SOP may locate all forms associated with this procedure at http://erinternal.lanl.gov/Quality/ user/forms.asp.

Attachment A: Laboratory Data-Validation Qualifier Flags, 1 page

Attachment B: Gamma Spectroscopy Data-Validation Reason Codes, 2 pages

Attachment C: Data-Validation Cover Sheet, 1 page

Attachment D: Gamma Spectroscopy Data-Validation Checklist, 1 page

Attachment E: List of Acronyms and Abbreviations, 1 page

Attachment A: Laboratory Data-Validation Qualifier Flags

R   The analyte is classified "rejected."

J   The analyte is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

J+   The analyte is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias.

          The analyte is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias.

U   The analyte is classified "not detected."

UJ   The analyte is classified "not detected" with an expectation that the reported result is more uncertain than usual.

Attachment B: Gamma Spectroscopy Data-Validation Reason Codes

Code	Rad	Qualifier Nondetects	Qualifier Detects	Description	Comments
4	R4	R See comments	R See comments	Required method blank documentation is missing. Validation cannot proceed without this information.	Package should be returned to the SMO or the information requested from the laboratory.
4a	R4a	N/A	U	Results for the affected analytes are considered not detected (U) because the associated sample concentration was less than 5 times the amount in the method blank.	
5	R5	U	U	Results for the affected analytes are considered not detected (U) because the associated sample concentration was less than the MDC.	
5a	R5a	R See comments	R See comments	MDC documentation is missing. Validation cannot proceed without this information.	Package should be returned to the SMO or the information requested from the laboratory.
5b	R5b	R	R	Results for the affected analytes are rejected (R) because spectral interference prevents positive identification of the analytes.	
6	R6	R See comments	R See comments	LCS documentation is missing. Validation cannot proceed without this information.	Package should be returned to the SMO or the information requested from the laboratory.
6a	R6a	N/A	J+	Results for the affected analyte are considered estimated and biased high (J+) because the associated LCS was greater than 120%R.	Qualify only detected results.
6b	R6b	R	R	Results/reporting limits for the affected analytes should be regarded a rejected (R) because the associated LCS was less than 10%R.	
6c	R6c	N/A	J-	Results for the affected analyte are considered estimated and biased low (J-) because the associated LCS was less than 80%R but greater than or equal to 10%R.	Code is used for detected analytes.
6d	R6d	UJ	N/A	Reporting limits for the affected analyte are considered estimated (UJ) because the associated LCS was less	Code is used for nondetected analytes.

Code	Rad	Qualifier Nondetects	Qualifier Detects	Description	Comments
				than 80%R but greater than or equal to 10%R.	
7	R7	UJ	J	Duplicate documentation is missing. Validation can proceed without this information with qualification.	Package should be returned to the SMO or the information requested from the laboratory.
7b	R7b	N/A	J	Results for the affected analytes are qualified as estimated (J) because the associated duplicate sample has a DER greater than or equal to 2 but less than or equal to 4.	
7c	R7c	N/A	R	Results for the affected analytes are qualified as rejected (R) because the associated duplicate sample has a DER greater than 4.	
9	R9	UJ	J-	Results/reporting limits for the affected analytes are considered estimated and biased low (J-)/estimated (UJ) because the extraction holding time was exceeded.	
9a	R9a	R	R	Results for the affected analytes are considered rejected (R) because the sample extraction exceeded 2 times the method published holding time.	
11	R11	N/A	U	Results for the affected analytes are considered not detected (U) because the associated sample concentration was less than 3 times the total propagated uncertainty.	Code should only be used after checking the detection status for results greater than the MDC except in cases where an MDC was not provided.
19	R19	See comments	See comments	Validator identified quality deficiencies in the reported data that require qualification. Please see the Data-Validation Cover Sheet for specific details.	Apply the appropriate qualifier to identify the effect of the quality deficiency on the reported data.

Attachment C: Data-Validation Cover Sheet

☐ Rejected Data

Section I

Request Number: _____ Validation Date: _____ Lab Code: _____

Contract Laboratory Name: _____

Validator: _____ Organization: _____

Analytical Suite (check all that apply): ☐ Volatile Organics ☐ High Explosives
☐ Semivolatile Organics ☐ Inorganics
☐ Organochlorine Pesticides/Polychlorinated Biphenyls ☐ Radiochemistry

Other (describe): _____

Section II—Completeness Check

Yes	No	n/a	(check one)	Yes	No	n/a	(check one)
☐	☐	☐	1. Chain-of-custody form(s)	☐	☐	☐	6. Raw/BSS data
☐	☐	☐	2. Case narrative	☐	☐	☐	7. Quality control forms
☐	☐	☐	3. Sample result forms	☐	☐	☐	8. Quantitation reports
☐	☐	☐	4. Sample chromatograms	☐	☐	☐	9. TICs forms
☐	☐	☐	5. Standard chromatograms	☐	☐	☐	10. TICs mass spectra

Identify any samples in the assigned Request Number that are missing:

_____ _____ _____ _____ _____ _____ _____ _____

_____ _____ _____ _____ _____ _____ _____ _____

Comments/problems noted (include information about requests for further information submitted to the contract laboratory and agreed-upon date of resolution and contract laboratory point of contact):

Validator's signature: _____ Date: _____

(Attach additional comment sheets as necessary.)

SOP-15.02, R1

Los Alamos National Laboratory
RRES-Remediation Program

Attachment D: Gamma Spectroscopy Data-Validation Checklist

Yes	No	n/a	(check one)	Assign qualifier listed below if criteria = Yes Detected analyte	Assign qualifier listed below if criteria = Yes Undetected analyte
☐	☐	☐	1. MDC and/or TPU were not stated for each radionuclide in each batch for each sample.	a	a
☐	☐	☐	2. Sample result is <MDC.	U, R5	U, R5
☐	☐	☐	3. Sample result is <3 times the TPU calculation.	U, R11	N/A
☐	☐	☐	4. Sample results are tentative because of spectral interference.	R, R5b	R, R5b
☐	☐	☐	5. Preparation/method blank is not reported.	R, R4	R, R4
☐	☐	☐	6. Analyte detected in blank <u>and</u> sample result for analyte =5x the amount in blank	U, R4a	N/A
☐	☐	☐	7. Duplicate analysis information is not present.	J, R7	UJ, R7
☐	☐	☐	8. DER for detected analytes is =2 but =4.	J, R7b	N/A
☐	☐	☐	9. DER for detected analytes is >4.	R, R7c	N/A
☐	☐	☐	10. Laboratory Control Sample (LCS) information is not present.	R, R6	R, R6
☐	☐	☐	11. LCS % recovery is >120%.	J+, R6a	N/A
☐	☐	☐	12. LCS % recovery is <80 but =10%.	J-, R6c	UJ, R6d
☐	☐	☐	13. LCS % recovery is <10%.	R, R6b	R, R6b
☐	☐	☐	14. Sample was extracted outside of the appropriate hold time.	J-, R9	UJ, R9
☐	☐	☐	15. Sample was extracted >2 times the appropriate holding time.	R, R9a	R, R9a
☐	☐	☐	16. Other obvious data quality issues identified.	__, R19	__, R19

a If the laboratory cannot provide the missing MDC, an estimated MDC can be calculated using 3 times the TPU.

Los Alamos National Laboratory
RRES-Remediation Program

SOP-15.06, R1

Attachment E: List of Acronyms and Abbreviations

CLP   Contract Laboratory Program (EPA)

COC   chain of custody

COPC   Contaminant of Potential Concern

DER   duplicate error ratio

DLC   decision level concentration

EPA   U.S. Environmental Protection Agency

ER   environmental restoration

FSF   Field Support Facility

LANL   Los Alamos National Laboratory

LCS   laboratory control sample

n/a   not analyzed

%R   percent recovery

QC   quality control

QP   quality procedure

ER   replicate error ratio

RN   request number

σ sigma (standard deviation of a set of measurements)

SMO   Sample Management Office

SOP   standard operating procedure

SOW   statement of work

TPU   total propagated uncertainty